# Studies in the Hydrolysis of Metal Ions 33

## A Miniature Solubility Column and its Application to a Study of the Solubility of Red Mercury(II) Oxide in Acid 3 M NaClO₄ Solutions

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A scaled-down version of a conventional solubility column which uses only about 2 g of solid material is described. It is well-adapted for handling radioactive materials, and has been used for radiochemical measurements of the solubility of red mercury(II) oxide in 3 M NaClO₄ solutions in the pH range 1—5.

Our results compare favorably with those of Garrett et al.[1,2], who obtained equilibrium by shaking for three weeks followed by settling for three to five days. Further improvements in the present method are proposed.

The presence of $Hg^{2+}$, $HgOH^+$, and $Hg(OH)_2$ as the only mercury-containing species is confirmed, and the following values for the equilibrium constants have been calculated:

$$\log {}^*K_1 + \log {}^*K_2 = -6.44 \pm 0.08$$
$$\log {}^*K_1 - \log {}^*K_2 = -0.30 \pm 0.30$$
$$\log K_{s2} = -3.75 \pm 0.01$$
$$\log {}^*K_{s0} = +2.69 \pm 0.10$$

where

$${}^*K_1 = [HgOH^+][H^+][Hg^{2+}]^{-1}; \quad {}^*K_2 = [Hg(OH)_2][H^+][Hg(OH)^+]^{-1};$$
$$K_{s2} = [Hg(OH)_2] \quad ; \quad {}^*K_{s0} = [Hg^{2+}][H^+]^{-2}.$$

M easurements of the solubility of sparingly soluble substances have traditionally been made by shaking samples of the solid and solvent together for periods long enough for equilibrium to be attained, and thereafter analysing the liquid phase, usually after separating it from the solid. Alternatively, and more conveniently, the solvent may be allowed to percolate slowly through a vertical column of the solid phase. The dimensions of this are not critical, but are usually chosen generously with a bed 20 cm or more in depth and perhaps 2 cm in diameter. Such a column requires a large amount of material, possibly too large if a radiometric method is to be used for the analysis of the

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solution, since in some cases it may be essential to use a solid phase with a high specific activity. While smaller quantities are needed for the first method, manipulative difficulties in separating the phases may also become important. A method of avoiding these and other problems by precipitating the solid from an active solution and measuring the reduction in the activity of the latter has recently been described [1].

In this work, we have sought to adapt the column method for use with small quantities of active solid by reducing the dimensions of the solid bed. Because of the general interest of this laboratory in hydrolysis, attention has been directed towards the possibility of measuring the solubility of oxides by a radiochemical method in a column of small size, and, for the initial experiments described here, mercury(II) oxide has been selected. It has a convenient isotope, [203]Hg, half life 47 days, and the hydrolytic processes undergone by Hg(II) are of considerable interest.

The solubility of both red and yellow mercury(II) oxides as a function of the hydrogen ion concentration was the subject of a careful study by Garrett and Hirschler [2] (alkaline solutions) and by Garrett and Howell [3] (acid solutions) who used the first method mentioned above, and an electrometric method of analysis of the mercury content of the solution phase. The technique now usual in studies of equilibria, of using a medium of high and constant ionic strength as the solvent, was not used, and the interpretation of the results is therefore complicated by the necessity of allowing for changes in the activity coefficients of the ionic species present. They concluded that, in acid solutions, $Hg^{2+}$, $HgOH^+$ and $Hg(OH)_2$ only were present, that the neutral species predominated over a wide range of hydrogen ion concentrations on either side of neutrality, and that, in sufficiently alkaline solutions, $Hg(OH)_3^-$ was formed. There was no evidence for the formation of $Hg(OH)_4^{2-}$ even in 2 M sodium hydroxide solution. Any polymer species present of the type $Hg_m(OH)_{n+2m}$ would not, of course, be detected by solubility measurements alone, but the general correctness of this hydrolysis scheme in acid solutions was later confirmed by Hietanen and Sillén [4] for a 0.5 M sodium perchlorate medium. They used the potentiometric titration method and concluded that $*K_2$ was smaller than $*K_1$, these constants being defined as:

$$*K_1 = [HgOH^+][H^+][Hg^{2+}]^{-1} \qquad (1)$$
$$*K_2 = [Hg(OH)_2][H^+][HgOH^+]^{-1} \qquad (2)$$

Clearly, sufficient is known about the hydrolysis of Hg(II) to make it possible to decide whether the method adopted for measuring solubilities gives essentially reasonable results, while, at the same time, a fresh study of the variation of the solubility of mercury(II) oxide with hydrogen ion concentration in a medium of constant ionic strength is not undesirable. This paper describes the results of solubility measurements at 25°C on the red form of mercuric oxide in acid sodium perchlorate solutions of $I = 3$, carried out in a miniature solubility column, the mercury analyses being done radiochemically.

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## Correction to "A Miniature Solubility Column and its Application to a Study of the Solubility of Red Mercury(II) Oxide in Acid 3 M NaClO₄ Solutions" *

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A systematic error in the $-\log[H^+]$ values quoted in this paper, arising from an arithmetical error, has been detected. Throughout they should be reduced by 0.142 units, e.g., all points in Fig. 2 should be shifted 0.142 units to the left and $-\log[H^+]$ at the intersection of the asymptotes in Fig. 2 should be 3.08 not 3.22. As a result, the published equilibrium constants must be altered as follows:

$$\log {}^*K_1 + \log {}^*K_2 = -6.16 \pm 0.08$$
$$\log {}^*K_{s0} = 2.41 \pm 0.10$$

This new value of $(\log {}^*K_1 + \log {}^*K_2)$ agrees with Ahlberg's potentiometric value [1] within the expected limits of error. The values of $\log {}^*K_1 - \log {}^*K_2 = -0.30 \pm 0.30$ and $\log K_{s1} = -3.75 \pm 0.01$ remain unchanged.

In the calculation of the solubility product $(pK_{s0})$ of $Hg(OH)_2$, Lagerström's value [2] of $pK_w = 14.03$ was used. This is applicable to 3 *molal* solution of sodium perchlorate; the measured value for the 3 molar solutions used in the solubility work is 14.22 [3]. Using this and the revised value of $\log {}^*K_{s0}$, $pK_{s0}$ becomes 26.0.

1. Ahlberg, I. *To be published.*
2. Lagerström, G. *Acta Chem. Scand.* 13 (1959) 722.
3. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand.* 11 (1957) 1039.

## EXPERIMENTAL

*Preparation of materials.* Red mercury(II) oxide was prepared by dissolving redistilled mercury in concentrated nitric acid (Merck' p.a.), and evaporating the solution until a white "mercury(II) nitrate" precipitated. This was then heated at 400—500°C in an electric oven until all nitrogen oxides had been driven off. The resulting powder (dark red when hot, scarlet when cold) was washed by decantation with conductivity water at frequent intervals for about a week in an attempt to remove soluble matter and very fine particles of oxide (*cf.* Refs.[2],[3]). It was then drained, dried over silica gel, and a 2 g sample sealed in a quartz tube for irradiation in the Swedish reactor R 1. As HgO is a rather soluble oxide it was only irradiated for 3 h in a flux of $5.5 \times 10^{11}$ neutrons cm$^2$ sec$^{-1}$.

A concentrated solution of sodium perchlorate was prepared from chloride-free sodium carbonate (Merck p.a., selected sample) and perchloric acid (Kebo p.a.) by the method normally used in this laboratory. A stock solution of perchloric acid, about 1 M, was prepared from the concentrated acid, analysed with potassium bicarbonate, and used to prepare the following solutions:

a) 0.1 M perchloric acid, 2.90 M sodium perchlorate.
b) 0.01 M perchloric acid, 2.99 M sodium perchlorate.
c) 0.01 M sodium hydroxide, 2.99 M sodium perchlorate.

Solution (c) was prepared from the stock sodium perchlorate solution, and a carbonate-free solution of sodium hydroxide prepared from Kebo p.a. pellets. Solution (b) was used as a standard of hydrogen ion concentration, and, in mixtures with (c), for preparing solutions of suitable hydrogen ion concentrations down to about $10^{-5}$ M to feed into the solubility column. Solution (a) was used to prepare acid solutions with [H+] between $10^{-1}$ and $10^{-2}$.

*The solubility column.* This was a conventional, scaled-down solubility column with the form and dimensions shown in Fig. 1. The column was immersed in a thermostated water-bath which also served as a radiation shield. The internal diameter of the column was made small enough to give a bed of mercury(II) oxide about 2 cm thick when a 2 g sample was used; it was felt that a further decrease in diameter might lead to flow along the walls rather than through the powder bed, and that, with a viscous medium like 3 M sodium perchlorate, the resistance to fluid flow would become unduly large. The height was chosen so that the closure at A lay above the level of the thermostat liquid when the bottom of the column rested on the bottom of the thermostat. The solid was held on a sintered glass pad, made in the laboratory and of uncertain pore size.

A novel feature of the column, particularly convenient when radioactive solutions are being handled, was the small lift-pump which was placed at such a level that the powder bed was never denuded of solution. Introduction of a slow stream of nitrogen at the point shown permitted the effluent from the column of solid to be transported without contamination to a suitable reservoir. Cylinder nitrogen freed from oxygen by passage over heated copper, and washed successively with 10 % sulphuric acid, 10 % sodium hydroxide, and then twice with 3 M sodium perchlorate solution, was used for this, and also to saturate all solutions with nitrogen before adding them to the column.

It was recognised that full equilibrium might well not be achieved by passing the solution once through such a shallow bed, and, in the earliest experiments, the solution was circulated from the column into an upper reservoir whence it dripped through the solid bed again. This continuous circulation was interrupted from time to time to take samples from the upper reservoir. These experiments showed clearly the excessively large amount of active mercury carried through the column when it was first used, but it proved more convenient in the main part of the work to collect a definite amount of solution which had passed through the column, and to analyse it before deciding whether further passage over the solid was necessary. To increase the head of liquid, and hence the rate of flow, the reservoir in these experiments was made from a 50 ml burette whose tip passed through the rubber stopper closing the column at A. This closure was gas-tight, and the contents of the reservoir dripped into the column at the same rate as the solution passed through the solid bed. Between 5 and 10 ml of solution were always above the solid bed in the column, and the solution coming in from the reservoir had ample time
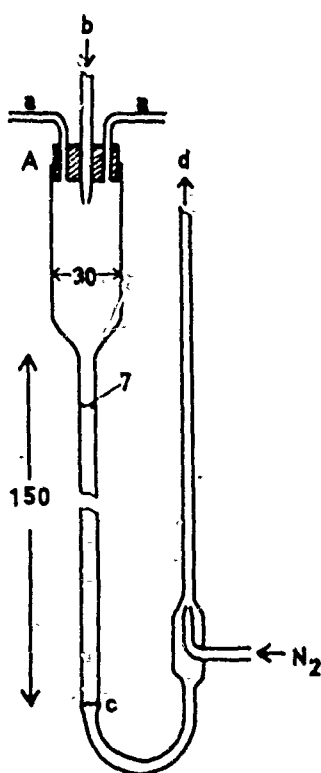
*Fig. 1.* Solubility column. All measures in mm.

a, a  Inlet and outlet tubes for passing nitrogen through top of column, and for reducing the pressure at this point when re-packing the column. Closed during normal operation of column.
b  End of reservoir-burette.
c  Sintered glass pad.
d  To collecting vessel

to reach temperature equilibrium with the thermostat since the flow rate amounted to only about 10 ml/h.

In the later experiments the following procedure was followed. A solution of the appropriate hydrogen ion concentration was prepared, and a stream of purified nitrogen passed through it for 20—30 min. It was then transferred to the burette reservoir and allowed to drip through the column. The first 10—15 ml coming over served to wash out the column and were discarded. The remaining contents of the system were collected, analysed, and returned to the column. Experiments at several different acidities (see below) showed that further small changes in concentration and acidity usually occurred up to and including the third pass through the column if this was working correctly, but that a fourth pass was not necessary. During the third and final run, at least two samples of 3—4 ml each were taken separately and analysed to check the homogeneity of the effluent and the reproducibility of the analyses.

The mercury content was found by taking a weighed sample of about 2 ml and counting the gamma radiation in a Tracerlab SC—57 low background well scintillation counter coupled to a SC—73 Versa/matic II Scaler. A standard mercury sample of known weight and of about the same volume was prepared from a solution made by dissolving about 0.04 g of the active oxide in approximately 1 ml of 3.5 M nitric acid and making up to 25 ml with solution (c). This was analysed chemically for mercury with potassium thiocyanate solution. This was itself standardised against a mercury standard prepared by dissolving an accurately known weight of pure mercury in 50 % nitric acid and diluting to a known volume. The mean of estimations was $6.35_1 \times 10^{-3}$ mole mercury per litre, with a standard deviation of $6 \times 10^{-4}$.

The acidity was measured with a Beckmann Red glass electrode connected to the silver-silver chloride reference electrode through a "Wilhelm" bridge, the complete cell being:

G.E. | Unknown solution | 3 M NaClO₄ | 2.99 M NaClO₄; 0.01 M AgNO₃ | AgCl, Ag

The e.m.f. of this was measured with a Radiometer pH meter, type 4. The reference electrode was prepared by Brown's method [1]. Hydrogen ion concentrations were calculated from the difference in e.m.f. observed when the glass electrode was immersed in solution (b) and in the solution under test; corrections for changes in the liquid junction potential with changing acidity were negligible in all solutions used.

To make these measurements, it was necessary to handle the solutions in the open laboratory which was not very desirable for solutions of low acidity since the buffer capacities were small, and it would be an improvement in future work of this kind to arrange to measure the acidity of the solution as soon after it leaves the solid as is possible. Another source of error in these acidity measurements was the small changes which occurred in the asymmetry potential of the glass electrode during the frequent washing and handling to which it was necessary to subject it. This, too, could be avoided by a modification of the kind suggested, and an improvement in the accuracy of this measurement would contribute appreciably to a reduction in the experimental scatter, and hence to an improvement in the precision with which the hydrolysis constants can be calculated.

## RESULTS

*Abnormally high "solubilities" in newly-prepared column.* The column was filled by adding the dry active mercury(II) oxide to the dry clean column, and passing in a nitrogen saturated solution. This was made up to be 2.99 M in NaClO₄, 0.01 M in NaOH, and was chosen for the preliminary experiments mainly because of Garrett and Hirschler's observation [2] that the solubility was nearly independent of the acidity in this range. For the first five samples taken the solution was being circulated continuously through the system. If it is assumed that:

i) full solubility equilibrium is attained in one pass through the column,

ii) the rate of flow out of the reservoir is equal to that through the column, it can be easily shown that the concentration $C_t$ in the reservoir at any time $t$ after the start of the experiment is related to the final steadystate value, $C_\infty$, by the equation,

$$C_t = C_\infty(1-\exp.(-t/\Theta)) \tag{3}$$

where $\Theta = v/V$. Here $v$ is the rate of flow, and $V$ the volume of the reservoir. The first of the above assumptions is not quite correct but this is not important for the present purpose. Table 1 shows some values of $C_\infty$ calculated from (3) and observed values of $C_t$, $t$, and $\Theta$. Samples 6—10 inclusive were obtained in subsequent experiments by direct sampling of the effluent from the column.

As can be seen, the apparent solubility of the oxide was highest for the earliest samples and fell as the total volume of liquid which had passed over the column increased. It was clear that the oxide sample was not completely uniform in spite of the prolonged washing it had received before irradiation. Had this been used in solubility measurements by the batch method, high and probably rather irregular values of the solubility would have been obtained, whereas by the column method it is easy to continue washing with a suitable solution until reproducible results are obtained.

*Table 1.* Apparent solubility of mercury(II) oxide in 0.01 M NaOH, 2.99 M NaClO$_4$ when the column is freshly packed.

| Sample | $t/\theta$ | $10^5\,C_{CO}$ M Hg |
|--------|-----------|---------------------|
| 1 | 0.2695 | 51.8 |
| 2 | 0.464 | 53.4 |
| 3 | 0.691 | 52.0 |
| 4 | 1.33 | 38.5 |
| 5 | 3.33 | 25.8 |
| 6 | Direct sample | 26.2 |
| 7 | ⸰ ⸰ | 25.2 |
| 8 | ⸰ ⸰ | 25.0 |
| 9 | ⸰ ⸰ | 22.9 |
| 10 | ⸰ ⸰ | 22.6 |

*The attainment of equilibrium.* After the preliminary conditioning made necessary by the high apparent solubilities observed with the freshly-packed column, it was found that the concentration of a solution which had passed once through the column could be increased slightly by passing it through a second time. Table 2 shows the changes in concentration of mercury and hydrogen ions when an initially mercury-free solution 0.01 M in perchloric acid and 2.99 M in NaClO$_4$ was passed four times through the column.

*Table 2.* Effect of repeated passages through the column of an initially mercury free solution, 0.01 M HClO$_4$, 2.99 M NaClO$_4$.

| No. of passes through column | Mercury concentration M × $10^{-4}$ | $-\log[H^+]$ |
|------------------------------|-------------------------------------|--------------|
| 1 | 41.3 | 2.57 |
| 2 | 42.0 | 2.58 |
| 3 | 43.4 | 2.57 |
| 4 | 43.0 | (2.54) |

In this case, and in several others which were studied, the third pass was necessary but not the fourth, and for this reason the experimental routine described earlier was adopted. From time to time, solubility values which were abnormally low compared with those expected from the provisional solubility curve drawn through the majority of experimental results, were obtained. These seemed to be due to some kind of mechanical defect such as channelling in the powder bed, since after reducing the pressure at the top of the column thereby sucking the powder back up it, and then allowing to settle again under gravity, normal results were obtained after two or three passes through the column. Some time would have been saved had this procedure been carried out more regularly.

A further point of practical importance is that it proved impossible to obtain satisfactory results by passing solutions through the column which
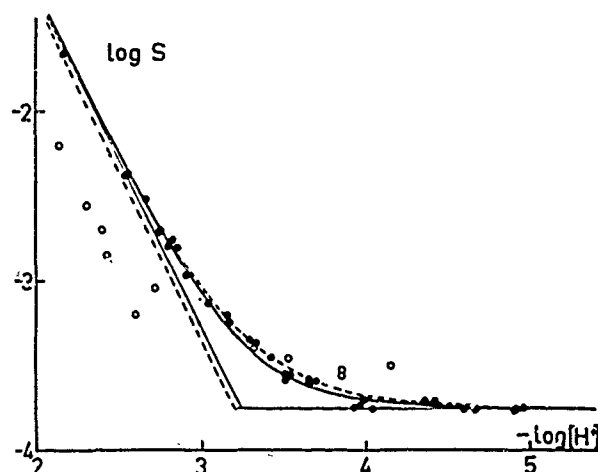
*Fig. 2.* Solubility results for red mercury(II) oxide in 3 M sodium perchlorate solutions.
● Experimental data reported in Table 3. O Garrett and Howell's data [3] in low and vari-
able ionic strength medium.

Full curve: Normalised solubility curve with $p = 0.50$ fitted to data.
Broken curve: Normalised curve with $p = 1$ fitted to data. The thin lines are the
asymptotes according to eqns. (7) and (8).

contained slightly more mercury than corresponded to their acidity. Repeated
passages failed to change appreciably either the mercury content or the acidity.
Two possible explanations are the presence of equilibria in the solution which
were attained very slowly, or more probably, the presence in the super-
saturated solution of mercury(II) oxide in a microcrystalline form which passed
through the column unchanged, and was analysed as soluble mercury.

*The solubility of mercury (II) oxide.* The results of the solubility measure-
ments, other than for those experiments in which solubility equilibrium was
demonstrably not attained, are shown in Table 3. Fig. 2 is a plot of log $S$
against log $[H^+]$ (filled circles) where $S$ is the concentration of mercury in the
solution, and $[H^+]$ is the free hydrogen ion concentration measured with the
glass electrode. Garrett and Howell's [3] values (open circles) for the solubility
of red mercury(II) oxide are also shown in this figure for comparison.

It can be seen that the change from a medium of very low ionic strength
as used by Garrett and Howell [3] to a 3 M $NaClO_4$ medium produces a very large
change in the solubility curve, while the reproducibility of the present results
can fairly be claimed to be better than that attained in their carefully designed
and executed experiments. It should be noted that their results as tabulated
represent the means of several different experiments carried out under the
same conditions, so that experimental variations have been smoothed out to
some extent in their data plotted in Fig. 2. The lower solubility for the neutral
species observed in the higher ionic strength medium is presumably a normal
"salting-out" effect. The charged species are "salted-in".

*Table 3.* The variation of the solubility of red mercury(II) oxide with hydrogen ion con
centration at 25°C in a 3M sodium perchlorate medium given as $-\log S$ ($-\log$ [H$^+$]).

    1.658(2.160),  1.357(2.165).
    2.302(2.569),  2.366(2.544),  2.362(2.544),  2.371(2.544).
    2.509(2.665).
    2.701(2.751),  2.698(2.758).
    2.752(2.845),  2.757(2.830),  2.767(2.835),  2.764(2.840).
    2.799(2.865).
    2.805(2.805),  2.799(2.802).
    2.968(2.900),  2.964(2.910).
    3.128(3.045),  3.124(3.045).
    3.203(3.155),  3.196(3.160),  3.201(3.155),  3.199(3.155).
    3.247(3.170),  3.246(3.170).
    3.334(3.296),  3.341(3.299).
    3.370(3.348),  3.360(3.339),  3.369(3.323).
    3.582(3.510),  3.554(3.554),  3.551(3.510).
    3.594(3.697),  3.603(3.658),  3.602(3.646),  3.603(3.660),  3.602(3.666),  3.605(3.646).
        3.582(3.668),  3.588(3.660),  3.582(3.650).
    3.761(4.050),  3.705(3.980),  3.705(3.950).
    3.747(3.930),  3.737(3.970).
    3.703(4.430),  3.701(4.375).
    3.751(4.672),  3.753(4.605).
    3.754(4.920),  3.761(4.920),  3.746(4.975).

Each group of results is derived from one independent experiment. They are included to show
the degree of variation between samples taken from the column at successive times.

## DISCUSSION

Both the earlier solubility work of Garrett and Howell [3], and the potentio-
metric study carried out by Hietanen and Sillén [4] could be interpreted on the
basis of the following equilibria:

$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+ \tag{4}$$
$$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_2 + H^+ \tag{5}$$
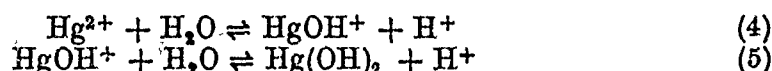
with equilibrium constants $*K_1$ and $*K_2$ defined by the eqns. (1) and (2) given
earlier. The formation of anionic complexes does not occur until the solutions
become strongly alkaline as can be seen from the solubility data of Garrett and
Hirschler [2]. In view of these results it can be assumed that the total dissolved
mercury $S$ in the acid solutions studied here is given by

$$\log S = [Hg^{2+}] + [HgOH^+] + [Hg(OH)_2]$$

which, from the definitions (1) and (2), leads to the equation

$$S = [Hg(OH)_2](1 + *K_2^{-1}[H^+] + *K_1^{-1}*K_2^{-1}[H^+]^2)$$

or

$$\log S = \log [Hg(OH)_2] + \log(1 + *K_2^{-1}[H^+] + *K_1^{-1}*K_2^{-1}[H^+]^2) \tag{6}$$

Log [Hg(OH)$_2$] is a constant if the solution is in equilibrium with the solid
phase, and the plot of log $S$ against $-\log$ [H$^+$] has two linear asymptotes.

When $*K_1^{-1}*K_2^{-1}[H^+]^2$ is large compared with $*K_2^{-1}[H^+]$ and unity, the asymptote has slope $-2$:

$$\log S = \log [Hg(OH)_2] - \log *K_1*K_2 + 2 \log [H^+] \qquad (7)$$

When both terms involving $[H^+]$ are much less than 1 it has a slope zero:

$$\log S = \log [Hg(OH)_2] = \log K_{s2} \qquad (8)$$

A standard curve-fitting technique, due to Sillén [6], has been used to determine the equilibrium constants. Plots of $\log (1 + pv + v^2)$ against $-\log v$ for values of the variable $v$ lying between 0.01 and 100, with $p = 0, 0.25, 0.50$, 1 and 2, were drawn and compared with one of $\log S$ against $-\log [H^+]$ derived from the experimental data, all plots being drawn to the same scale. By comparison of eqn. (6) with the normalized variable $Y = \log (1 + pv + v^2)$ we find

$$p = \sqrt{*K_1/*K_2} \qquad (9)$$

From values in Table 3 we calculated with eqn. (8)

$$\log S = -3.75 \pm 0.01 = \log K_{s2}$$

Using this value as the horizontal asymptote an acceptable fit to the experimental curve could be obtained with $p = 0.5$ and 1, $-\log [H^+]$ at the intersection point of the asymptotes being found as

$$-\log [H^+] = 3.22 \pm 0.04 = \tfrac{1}{2} \log *K_1*K_2$$

The deviation represents the limits within which this intersection could lie if the data are fitted to a curve with $p = 0.5$ or 1 (the curves are drawn in Fig. 2). Because of the experimental scatter, it is not possible to be very precise about the value of $p$. From Hietanen and Sillén's published constants [4], valid for a medium 0.5 M in sodium perchlorate, $p$ can be calculated as $0.28 \pm 0.05$ and recently Ahlberg [7] has obtained the preliminary value $p = 0.39$ for 3 M $NaClO_4$. The present solubility data are therefore not quite consistent with the potentiometric measurements, but the difference is not too serious.

The solubility of the neutral species $Hg(OH)_2$ is $K_{s2} = (1.77 \pm 0.05) \times 10^{-4}$ M, and $\log *K_1 + \log *K_2 = -6.44 \pm 0.08$, both values referring to a 3 M sodium perchlorate medium at 25°C. The latter value is somewhat smaller than Ahlberg's potentiometric value [7] $-6.22$ (preliminary) and the value $-6.30$ determined for 0.5 M $NaClO_4$ by Hietanen and Sillén [4].

Separate values of $*K_1$ and $*K_2$ can be obtained by combining this sum with the difference derived from the values of $p$ (eqn. (9)) which give the best fit to the curve. When $p = 1$, the two constants are equal, and when $p = 0.5$, $4*K_1 = *K_2$. We can therefore only obtain $\log *K_1$ and $\log *K_2$ separately with rather large errors: $\log *K_1 = -3.37 \pm 0.19$ and $\log *K_2 = -3.07 \pm 0.19$. Ahlberg [7] has obtained the preliminary values $-3.52$ and $-2.70$ and Hietanen and Sillén [4] $-3.70$ and $-2.60$. There is no doubt that at present a more accurate $p$ value is obtained by the potentiometric method.

The solubility product $*K_{s0}$ of $Hg(OH)_2$ can also be calculated from the relation $K_{s2} = *K_{s0}*K_1*K_2$ as $\log *K_{s0} = 2.69 \pm 0.10$. In 3 M $NaClO_4$ at

$25°C$, Lagerström[8] found $pK_w = 14.03$, and hence, the solubility product of $Hg(OH)_2$ $(pK_{s0})$ for these conditions is 25.4.

No other study of the solubility of mercury(II) oxide in a 3 M sodium perchlorate medium has been reported. Some old solubility measurements of Grossman[9] in a variable ionic strength medium at $25°C$ gave a value for $pK_{s0}$ of 25.4, and Latimer[10] calculated a value of 25.52 for an infinitely dilute solution. Garrett and Howell's[3] value for log $*K_{s0}$ at low ionic strength is 1.72 against the present one of 2.69 for 3 M $NaClO_4$. Their calculations of log $*K_1$ and log $*K_2$ were not done by curve-fitting methods, and they found $-2.49$ and $-2.85$, respectively, or log $*K_1*K_2 = -5.34$. These figures were based on solubility measurements of both red and yellow forms of mercury(II) oxide. Using only the data for the red oxide shown in Fig. 2, the curve fitting method gives a value for log $*K_1*K_2$ of about $-5.6$, but the values are too few to give any real estimate of the individual constants.

An important result of the present work is the conclusion that accurate solubility measurements can be obtained from the column method using a much smaller quantity of solid phase than is usually the case, the only penalties being the necessity of passing the solution through the column two or three times, and of frequent re-packing of the column by the simple technique described. This modified column method, with the technique of collecting samples using a small gas-lift pump, is well-adapted to handling radioactive materials, and could be safely used with a solid phase having a much higher specific activity than that employed here. This would be useful in studying substances of low solubility.

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